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FINAL REPORT

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INFORMATION

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APPLIED SCIENCE RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

FINAL REPORT

December 1, 1951 - October 31, 1953

ON

DEVELOPMENT OF NEW POLYMERS FOR AIRCRAFT APPLICATION
NAVY BUREAU OF AERONAUTICS
Contract NOas 52-090 c

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I. INTRODUCTION

The work which has been carried out on this project was concerned with the study of elastic polymers, particularly with respect to their suitability as a lacquer. Several copolymers of chloroprene were studied intensively. These copolymers were:

chloroprene-methacrylic acid
chloroprene-methacrylamide, and
chloroprene-acrylic acid

Other polymers which were tested for control purposes came from commercial sources. These were:

N-79 Aircraft Lacquer, Gates Engineering Company
1801-C, Goodyear's Top Coat Base Cement
Hypalon S-2, Du Pont's
"Coroguards" and "Teflon Tape", Minnesota Mining and
Manufacturing Company

A large part of the present research was devoted to the development of practical polymerization recipes. When these techniques were perfected, a study of conversions and polymer compositions was begun in order to determine the effect of these variables on physical properties and ultimately on rain erosion resistance. Next, effective cures were evolved which gave optimum physical properties to each copolymer. Physical properties of importance in this study were tensile strength, permanent set, permanent elongation at the breaking point, "creep" properties, and finally, rain erosion resistance. The study of the physical properties was necessary to evaluate the polymers and to point the direction in which effort should be concentrated.

II. EXPERIMENTAL

A. Chloroprene-methacrylic acid (CMA) copolymers

1. Preparation of Polymers

Most of the work on this project was devoted to the study of the CMA copolymer because of its excellent tensile strength and rubbery characteristics. This copolymer also showed favorable results in rain erosion tests at Cornell University which justified the further exploration of its possibilities. The work done previously in this laboratory indicated that a special technique of polymerization gave the most useful polymer. This particular polymerization was carried out by the usual emulsion technique in which citrate of magnesium bottles were charged with the reactants and rotated end over end in a thermostatted bath.

(a) Recipe

redistilled water	193g
Triton X-301	8.75g
K ₂ S ₂ O ₇	0.35g
Sulfur	0.291g
Monomers	96.2g
(Chloroprene	30.5g
(Methacrylic acid	65.5g

Nitrogen is blown through the bottles to exclude oxygen and the polymerization is carried out at $30^{\circ}\text{C} \pm .2^{\circ}\text{C}$ for about 1 hour 15 min. The desired conversion is obtained when the refractive index of the latex is 1.385. When the reaction is complete, an aqueous dispersion of hydroquinone and tetramethythyuram disulfide (Methyl tuads) is added to the latex as a shortstop.

After coagulating the polymer by freezing, the mass is cut into small pieces and dried in vacuo at 50°C . One part of phenyl B-naphthylamine and 2-1/2 parts methyl tuads per 100 parts of polymer are then milled into the dried polymer as an antioxidant and a plasticizer, respectively.

The Triton in the recipe serves as an emulsion stabilizer; however, 1-2g of precoagulum are obtained despite its presence. The sulfur modifier is used to give less cross-linking and consequently less gel. Hence, these modified polymers with slight cross-linking go into solution more readily and give a more homogeneous film than unmodified polymers. However, when modifiers are added to the polymer recipe, the chain lengths tend to be smaller and tensile strengths, in turn, are lowered. But with appropriate cures, this defect in tensile strength can be effectively corrected. The sulfur modifier acts as a chain breaking agent; that is, it invokes a transfer of the free radical from a chain end to itself and thus starts a new chain. Consequently, the chains tend to be smaller in length since their growing terminal groups are cut off prematurely. It is this removal of active centers which prohibits undesired cross-linking of chains.

(b) Conversions of Polymer

The problem of discovering the proper conversion which would give optimum strength and yet yield polymers with good solubility had to be solved before any effective coating could be developed. The extent of conversion can be altered by varying the polymerization time or temperature or by varying both at the same time. The sulfur modifier mentioned above, is also effective in changing the conversion values. It was found that the optimum conversion for the purposes at hand ranged from 52-60%. All of the rain erosion data which follows were based on polymers prepared with conversions ranging from 52-60%. By using a fairly constant value for conversion, curing procedures and solvent combinations were studied systematically. Since lower temperatures of polymerization give a more homogeneous polymer and one which has longer unbranched chains, 30°C was chosen as the most effective temperature.

(c) Composition of Polymer

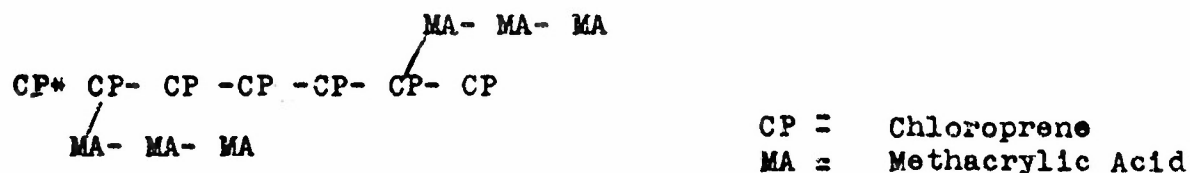
Methacrylic acid was used as a co-monomer in order to introduce a polar acid group and thus secure good adhesion to aluminum. However, as the acid content is increased, the resulting polymers become stiffer and less elastic. As a result, the rain erosion resistance is weakened; thus high acid content must be avoided. Acid percentages as high as 20% were found useful as primer coatings because of excellent adhesive strengths, although they made poor top-coats. Further variations in composition showed that acid ratios of 10-13% gave higher tensile strengths than pure neoprene and the rain erosion resistances of these polymers were comparable to neoprene. In order to obtain the above composition, the acid charge was 30.5g as is indicated by the recipe given above.

A second aspect of the composition is the manner in which the two monomers combine to form a copolymer. The true structure of the polymer has not been ascertained; however, it is known that chloroprene polymerizes alone at first. Then as the reaction approaches completion the methacrylic acid begins to polymerize. Fractional precipitation studies on chloroprene-methacrylamide show that the polymer is heterogeneous; namely, partitions are obtained which are essentially polychloroprene as indicated in table below.

Fraction	Wt.	TABLE I		intrinsic viscosity
		% Chloroprene	% soluble	
1	5.07	77	31	0.38
2	6.81	95	90	0.55
3	5.81	98	100	0.63
4	3.79	98	100	0.39
5	1.17	98	100	0.30

However, when polychloroprene and polymethacrylic acid or polymethacrylamide are mixed mechanically on a rubber mill, it is observed that these polymers are not compatible. Furthermore, step-wise addition of methacrylic acid to chloroprene yields a polymer which is similar in nature to the polymer obtained when the monomers are charged together. This step-wise addition is carried out by polymerizing chloroprene by itself and after the monomer is stripped off, methacrylic acid is added with more initiator, and polymerization is continued.

These facts point to the possibility that the material is actually a copolymer with the following structure:



That is, linear chains of chloroprene are formed initially, to which are attached shorter methacrylic acid chains as side branches. It is difficult to obtain a more homogeneous polymer because of the great reactivity of chloroprene, as compared to other monomers. An effort was made to achieve a more successful copolymer in the bulk phase, but the unbalanced reactivity ratios were the same and lead to the same type of copolymer.

The analysis of the copolymer can be carried out in either of two ways:

1 - Direct Method

The chlorine content is determined directly by the Volhard method. This method necessitates fusing the polymer with sodium peroxide in a Parr bomb whereby the chlorine is transformed to NaCl which is easily determined.

2 - Indirect Method

A 10 g sample of latex is removed and coagulated separately.

Since the total acid in this sample is known from the ratio in the

original charge, it is possible to calculate the acid content of the polymer by subtracting the amount of monomeric acid left in the latex solution. The chloroprene content is then calculated by subtraction. The two methods give results which check with each other within 1-2%. The Volhard titration gives results consistently 2% lower than theoretical so that the acid titration probably is more accurate.

(d) Compounding

(1) Cures - After a suitable polymer is obtained, it is necessary to utilize efficient curing agents in order to achieve optimum cures. The rain erosion resistance of polymers is highly dependent upon the type of cure. This dependence is shown by a comparison of rain erosion data versus curing. (See data on Cornell Tests.) When 1% magnesia (MgO) is added to a polymer solution, one of the best cures for CMA polymers is realized, since by this procedure tensile strengths up to 5,000 psi have been obtained. However, this metallic oxide is insoluble in the lacquer and is partially incompatible with the polymer. As a result, a heterogeneous surface is obtained which causes the coating to fail at arbitrary points owing to imbedded granules of MgO . This type of behavior is not representative of true erosion and is not suitable for comparison with other types of coatings. Consequently, a search for compatible accelerators led to the use of organic agents. The organic compounds which proved to be most effective in securing high tensile strengths were organo-metallic compounds such as ethyl zimate (zinc diethyldithiocarbonate) and aromatic diamines, such as diaminodiphenylmethane (DADPM). The excellent tensile value of 5750 psi was obtained by using 10 parts ethyl zimate and 2 parts of DADPM per 100 parts of polymer. In addition, this curing system with CMA gave a coating which lasted 30 min. in the Cornell tester.

Up to the time of the 10th Cornell series, the best performance of CMA in the test was 60 min. of exposure and in this case the curing agents were 2 ml 983-C (Goodyear)/2 gm polymer plus 4 parts of DADPM /100 parts of polymer. Not only are these curing agents soluble in the solvent system, but they are also compatible with the polymer as evidenced by the absence of "bloom". Thus, a more homogeneous coating of moderately high tensile strength was obtained which resists rain erosion more successfully. This is an example of good surface properties overshadowing the requirement for good structural strength.

At first, the specimens were heated for 1 hour at 120°C in order to achieve a successful cure. However, in order that the lacquer be adaptable to actual service conditions, a short air cure is most desirable. For this reason, most of the later work was confined to cures which could be effected at room temperature. In this regard, the CMA polymer which was most effective in resisting erosion was specimen 9 I (60 min.) which was cured at room temperature for 21 days. At the end of this time, the tensile strength was 3,200 psi.

(2.) Other Additives - Other agents can be added as fillers to CMA gumstock to get better physical properties. It is well known that carbon black when added to rubber stocks increases their abrasion resistance appreciably. However, in all cases where filling was attempted, the unloaded vulcanizate proved to be more resistant to rain erosion. This is another example of a more homogeneous polymer giving a better erosion resistant coating despite any other benefits which the added material may impart. The 9th and 10th Cornell series illustrate the harmful effects of adding carbon black and hydrophobic silica, both of which materials give improved properties to other polymers.

(e) Physical Properties of the Polymer

(1.) Tensile Strength - A study of physical properties was initiated

in order to screen the various polymers and cures before sending the specimens to Cornell. In this way, the obviously inferior specimens could be discarded to reduce the number of specimens to be tested. Of greater importance was the study of possible correlations of physical properties of elastomers with rain erosion resistance. If some correlation of data were possible, greater insight into the problem of preventing rain erosion might result. It would seem that the polymer with the highest tensile strength should have better rain erosion properties, other things being equal. This condition is observed only for extreme cases yet not with strict consistency. Moreover, some of the coatings with the highest tensile strength failed early. For instance, the MgO cures which effect high tensiles do not achieve erosion resistance. In this case, it is suspected that the heterogeneity of the cured specimen causes points of weakness to develop. Possibly also, a tight cure, while giving high tensile data, causes a decrease in elasticity which will show up in low elongation at the breaking point. Hence, there has been no observable correlation between rain erosion properties and tensile strength of the cured polymers.

(2.) Permanent Set and Elongation - A study of the elongation at the breaking point and the permanent set properties of the specimen give an indication of its elasticity. Intuitively, it seems probable that a coating with high tensile strength combined with good elasticity will resist rain erosion for a considerable time. In general, this premise has been proven correct in that polychloroprene and the CMA copolymers have been moderately successful in these tests. Yet, even within a series of panels, no direct correlation can be shown between elastic properties and rain erosion resistance. In fact, Goodyear's 1801-C coating has a very high permanent set but excellent erosion resistance. In comparison, Gates N-79 coating, with a proper cure,

has equal rain erosion properties but low permanent set. In addition, not even a series of CMA coatings show a systematic dependence of physical properties with erosion as shown by Table II.

(3.) Creep - The study of "creep" properties of elastomers was introduced to compare erosion data with this fundamental property of a polymer. It is possible to study the "creep" function by applying a constant stress on the specimen and recording the time dependence of the resulting deformation. This elastic deformation is the result of three distinct effects, ordinary or instantaneous deformation, configurational or retarded deformation, and viscous flow. The last feature, viscous flow, is a non-reversible property which gives rise to permanent set. That is, the film will not retract to its original length over long periods of time. Plastic deformation can be represented by a mechanical model. (reference)

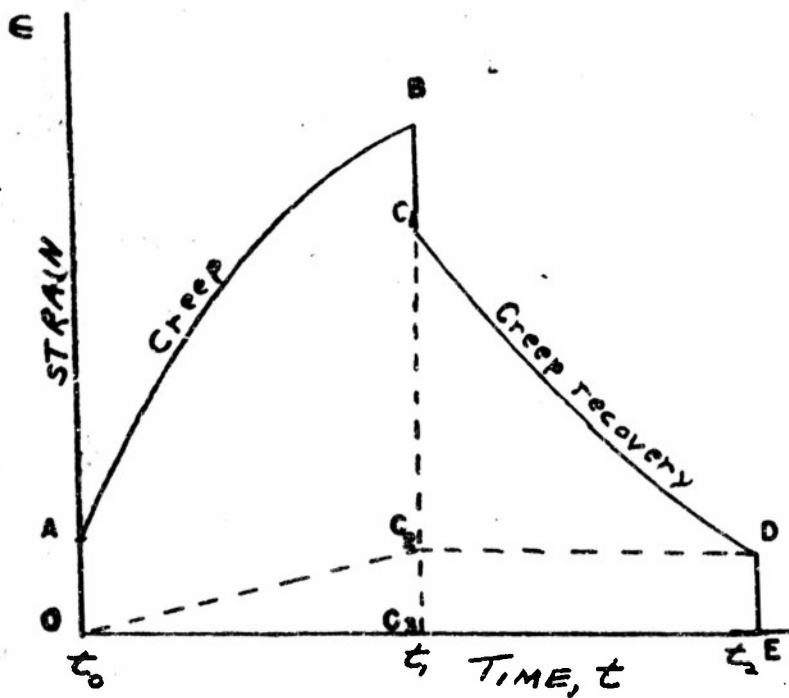
When calculated by using these theoretical mechanical equivalents, the "creep" function gives graphs quite close to actual creep curves up to an elongation of 500%. If a better fit is required at higher elongations or for a particular polymer, additional retarded elements can be added to the diagram, Fig.I. For CMA copolymers, 4 retarded elements were desired to get meaningful data. The instantaneous deformation OA is likened to the action of steel spring and the retarded deformation can be compared to the action of a piston and spring in parallel. The latter recovery, $E_2 + C_1C_2$ is reversible but time dependent, as shown by the diagram, while the viscous flow C_2C_3 is non-reversible and can be represented merely by the viscous action of a piston N_1 .

Because the creep function is a more meaningful criterion of elastic behavior than set and elongation alone, it was felt that a better correlation of such data with rain erosion resistance could

TABLE II

Physical Properties of Rain-Erosion Specimens

Panel No.	Time to Erode Thru	Total Test Time	Tensile Strength	% Elong. at break	ASTM set
			psi		
8C	15	20	4570	680	31
8L	40	45	5100	-	-
8K	20	30	5430	-	-
8I	80	90	2000	690	126
8J	60	60	2800	700	20
9D	peeled at 10	50	7930	560	13
9E	30	50	2310	1070	51
9I	60	80	3150	1020	25
9J	20	50	6020	790	20
10A	60	140	3060	-	-
10B	80	235	3520	900	15.5
10C	40	100	4150	-	-
10K	76	96	3200	-	-
10D	10	15	5780	650	43



$E = E_{\text{elastic}} + \text{retarded} + \text{Viscous}$
elastic deformation

$$= E_H + E_R + E_V$$

$$= BC_1 + C_1 C_2 + C_2 C_3$$

$$= \frac{S}{E_1} + \frac{S}{E_2} \left(1 - e^{-\frac{E_2}{\eta_2} t}\right) + \frac{S}{\eta_1} t$$

$$= \frac{S}{E_1} + \frac{S}{E_2} \left(1 - e^{-t/\lambda_2}\right) + \frac{S}{E_1} \left(\frac{t}{\lambda_1}\right)$$

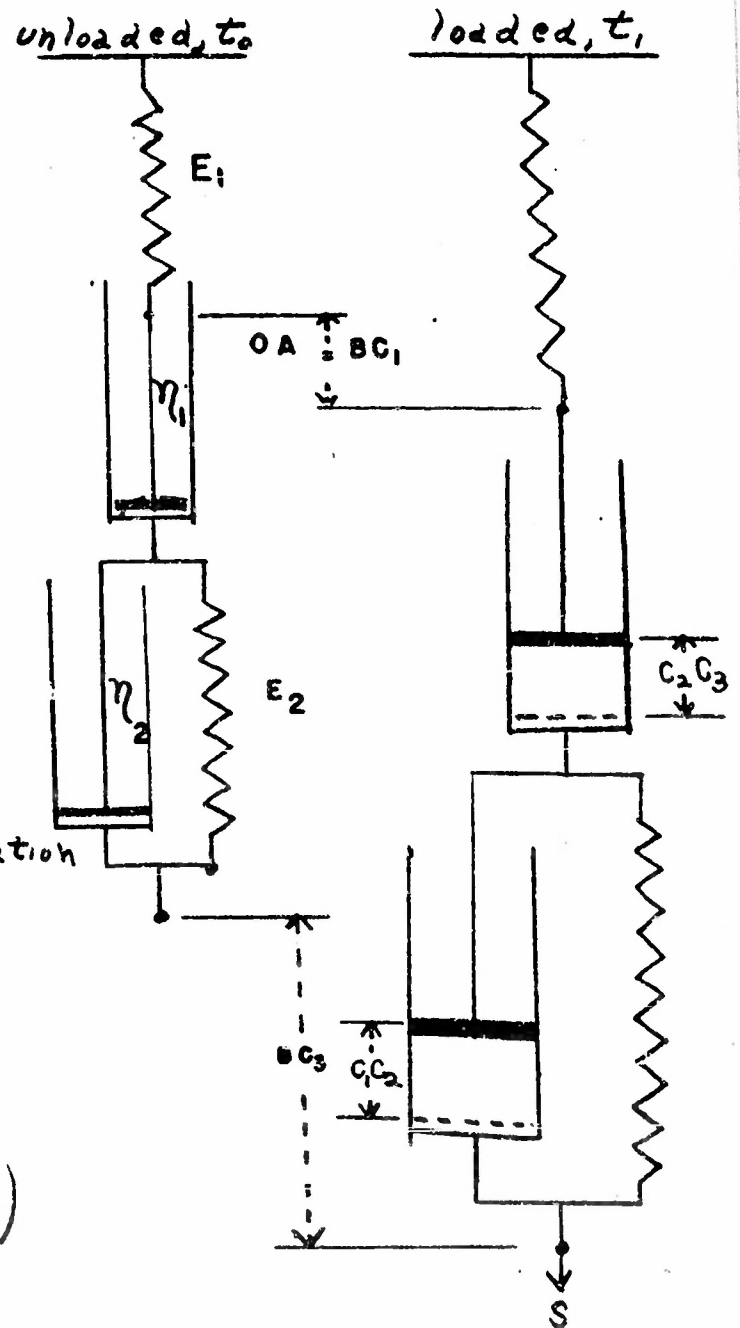


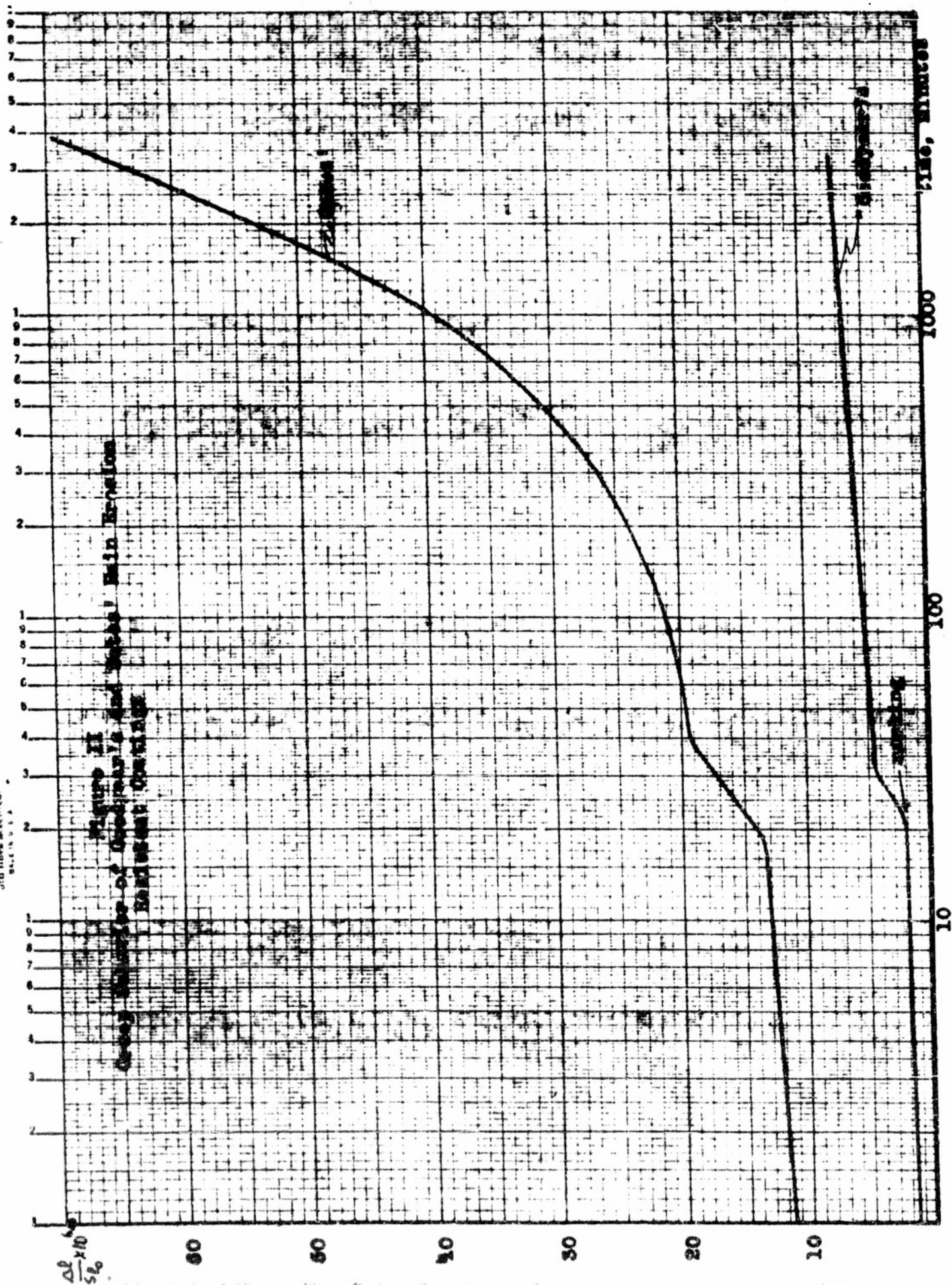
Figure 1

be made. However, experimental evidence shows that creep data also suffer from the same limitations exhibited by our other physical tests. Fig.II shows that even though Gates and Goodyear exhibit different visco-elastic properties, their rain erosion resistances are of the same order of magnitude. Furthermore, it is known that an increased loading of hydrophobic silica will reduce the compliance of a polymer considerably, yet no significant change in erosion resistance has been shown.(Figure III) Another example of the lack of correlation is the low compliance of Goodyear's and Gate's coatings as opposed to 9F of the Cornell series which had a high compliance; yet 9F exhibited rain erosion properties comparable to the commercial coatings. (Figure IV) Other specimens of lower compliance failed earlier in the testing so these results show that "creep" studies likewise fail to give an insight into the rain erosion properties of a given polymer.

(4.) Miscellaneous Properties - An interesting but unfortunate characteristic of the CMA copolymer is its tendency to form a blistered surface when immersed in water for 24 hours. It is believed that these bubbles are loci for rain erosion attack and that they cause flaking off of the polymer at arbitrary spots rather than gradual erosion. Films cured with MgO do not show this blistering but, in this case, dispersed particles, which can be seen with a 50X microscope, are the suspected loci of erosion. As a result of these complicating factors, data from physical tests still do not show how a film will behave under actual testing.

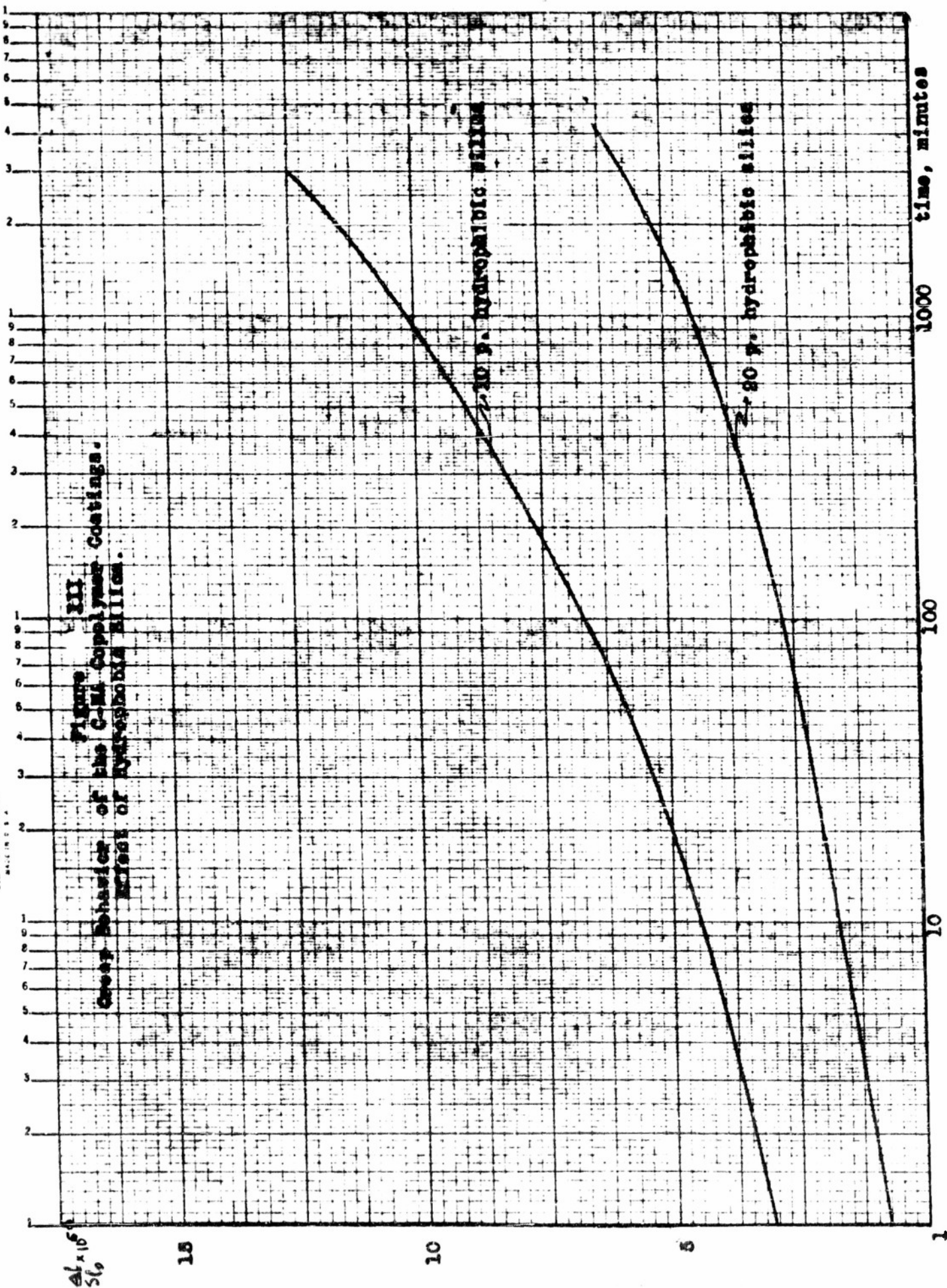
A study of the low temperature characteristics of various copolymers indicates that CMA copolymers are poorer than Hevea and neoprene.

250-01 GEORGE & CO. CO.
Semi-Logarithmic, 4 Cycles X 10 to the inch.
5th lines included.
Scale 10 to 1



138 91 KEUFFEL & ESSER CO.
2-in. logarithmic, 4 Cycles X 10 to the left
5th lines accented

III
Creep Behavior of the C-M Copolymer Coatings.
Effect of Hydrophobic Silica.



100-81 KUFFEL & ESSER CO.
Semi-Logarithmic, 4 Cycles X 10 to the inch.
All lines corrected

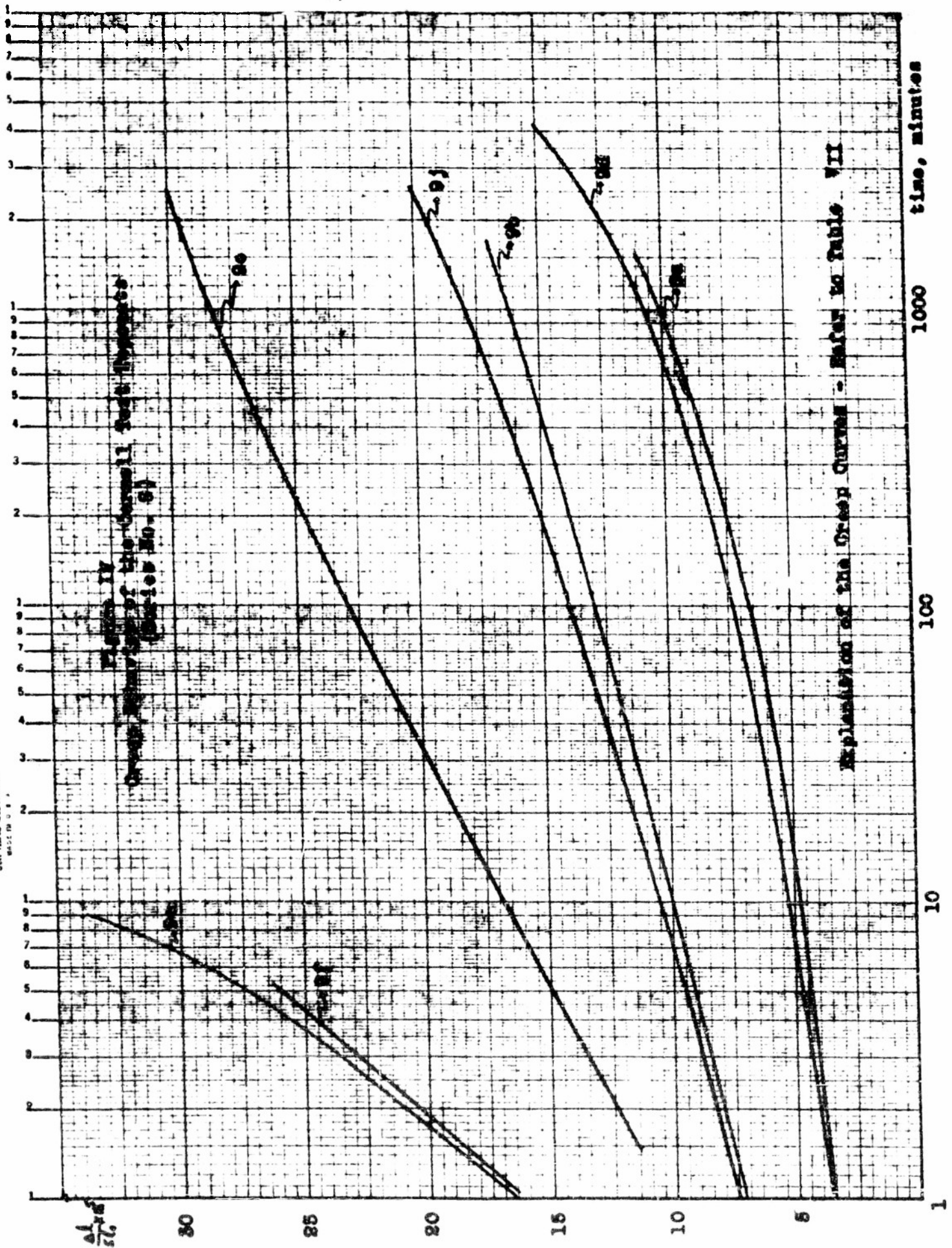


TABLE III

Comparison of Low Temperature Properties* of Polymers

<u>Polymer</u>	<u>Temperature, °C</u>	<u>Percent Retraction</u>			
		<u>-10</u>	<u>-30</u>	<u>-50</u>	<u>-70</u>
hevea	-54.2°C	-29.6	-11.1	-5	
neoprene	-40.4	-35.2	-24.6	3.6	
CMA	-12	- 8	- 5	-1	
chloroprene- methacrylamide	-33	-29	-10	9	
chloroprene- acrylic acid	-30	-22	-10	1	

*Films elongated 250% and conditioned 10 min. at -65°C

This table shows that CMA polymers would not behave elastically at moderately low temperatures (-20°C) and rain erosion resistance would suffer upon cooling. However, rain isn't encountered at low temperatures so this drawback may not be too serious.

A more serious deficiency of the chloroprene polymers is their tendency to decompose and liberate hydrochloric acid when subjected to ultra violet light. The acid is leached out of the coating by the rain and proceeds to destroy the aluminum. This corrosive action seriously impairs the utility of chloroprene copolymers as rain resistant coatings, unless of course the decomposition can be avoided. However, when basic reagents are added to a polymer, its rain erosion resistance is lowered. If any future work is to be done on chloroprene copolymers, it will be necessary to stabilize the polymer without affecting its toughness. Phenyl B-naphthylamine is a possible stabilizing agent which can inhibit the degradation of the polymer and it has been employed in some of the present work.

B. Other Polymers of Chloroprene

1. Chloroprene-methacrylamide

Of all the coatings prepared by this laboratory, the methacrylamide copolymer when properly cured gave the best protection against rain erosion. Samples 10A and 10B in the Cornell tests lasted 60 and 80 minutes respectively; moreover, this behavior was achieved with curing agents producing the moderate tensile strengths of 3,060 and 3,520 psi. respectively. The Goodyear 983-C accelerator was used as the curing agent, but when a MgO cure was used, a resistance of only 40 min. was recorded despite the higher tensile value of 4150 psi. owing to the deleterious effects of MgO particles on the surface of the film. A feature of considerable importance is that curing continues up to 2 weeks after the actual baking so a conditioning period must precede any physical tests. Also, before formulation for the cure takes place, a sufficient milling time must be allowed to achieve good solubility and tensile strengths.

TABLE IV

<u>Milling Time</u>	<u>% Solubility</u>	<u>Tensile Strength</u>
4 (min.)	63	3730 (psi)
6	79	3600
8	84	3890
10	91	4330
12	99	4370

The details for the production of methacrylamide copolymers are not given here because of their similarity to the procedures used for CMA copolymers.

2. Chloroprene-acrylic acid copolymer

The acrylic acid homologs were not investigated thoroughly because of their poor preliminary showing in comparison to the results

obtained from CMA and chloroprene-methacrylamide. No favorable tensile data were obtained with these polymers and the elastic properties were also unfavorable.

C. Commercial Polymers

1. 1801-C Top Coat Base Cement

A series of polymers from commercial sources were run as a control in the rain erosion tests. The best of the commercial polymers was Goodyear's Top Coat Base Cement 1801-C. However, this chloroprene-base lacquer did not show the high tensile strengths and elasticity characteristic of the polymers produced in the present study. It is likely that the chief reason for the success of 1801-C is its ease of application and the smooth homogeneous surface which is obtained. These properties are not measurable as yet but they are of great importance in protecting against rain erosion.

2. N-79 Aircraft Coating

The Gates Engineering Company's N-79 lacquer is another material which has performed successfully in rain erosion tests. It gives slightly higher tensile strengths than Goodyear's coating but still doesn't compare with CMA in this respect. Its set properties are more favorable than Goodyear's and its top performance in erosion tests compares favorably with that of the Goodyear polymer. Here too, the smooth coating which is produced probably greatly enhances its resistance.

3. Hypalon S-2

Du Pont's Hypalon S-2, which is a chlorosulfonated polyethylene, does not give satisfactory test results. Not only are its physical properties unfavorable in comparison to CMA but it gives a rougher, grainy coating from methyl ethyl ketone and toluene solvent combination. Hence, when CMA coatings are compared to a coating with similar surface appearances, the CMA is superior in rain erosion resistance.

4. Coroguard

Of special interest is Minnesota Mining and Manufacturing Company's "Coroguards". These coatings are now being used by military aircraft for protection against rain erosion and it seems that they give satisfactory results. Yet when these polymers were tested on the Cincinnati Rain Erosion tester, the results were entirely unfavorable. The best specimen tested survived for only 2 minutes. These coatings were sprayed on the panels by a representative of the company according to company specifications. Most of the specimens were smooth but were non-elastic in nature while seemingly quite durable. However, time limitations prevented the natural weathering of the specimens, contrary to actual procedure used in aircraft preparation. As a result, a true comparison with actual flight conditions can not be made as yet. At the present time, several specimens are being weathered for 3 months. At the end of this time, the "coroguard" coatings will be re-tested.

5. Teflon Pressure Sensitive Tape

Another Minnesota Mines and Manufacturing product which has been tested is Teflon Adhesive tape. Teflon, polytetrafluoroethylene, has very high tensile strength and good toughness in addition to being chemically inert. The main objection to this material is its lack of elasticity. As a result of this deficiency, the material failed within 15 seconds. The material was very smooth and apparently homogeneous; its adhesion to the metal was sufficient to give a true erosion pattern. The Coroguards do not show good elastic properties and like Teflon they failed quickly in the tests. Thus, a non-elastic material, despite high tensile strength and toughness, fails because it cannot absorb the energy of deformation reversibly. That is, instead of springing back and releasing its energy, the material absorbs the energy in its bonds which subsequently rupture, causing

the material to fail.

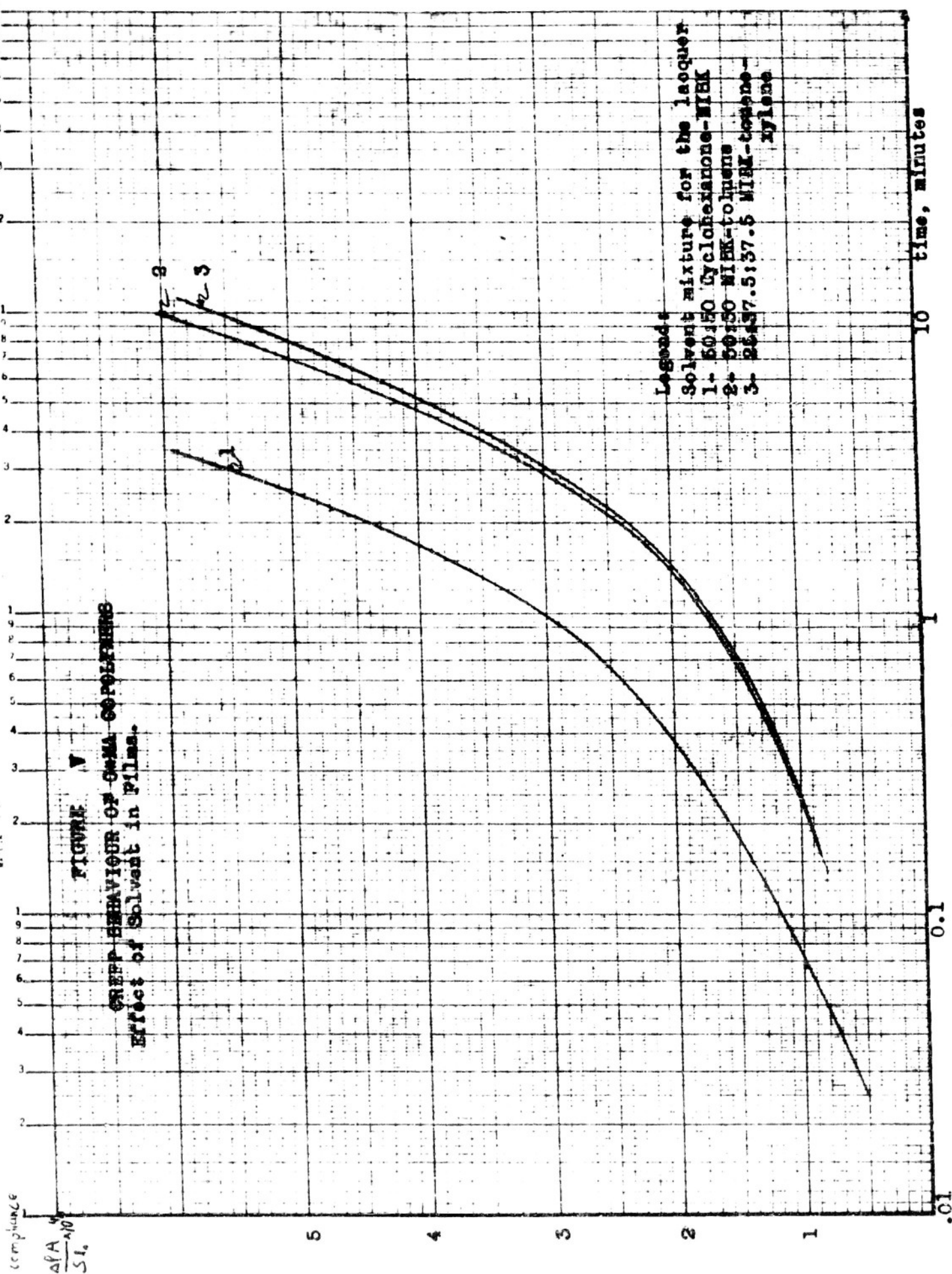
D. Lacquer Properties

1. The Solvent System

In order to get a suitable lacquer with good application characteristics and homogeneity, it is necessary to choose the proper solvents. The best solvent, so far, for CMA is cyclohexanone. Methyl isobutyl ketone is another good solvent for these polymers, and a typical solvent system consists of 50% methylisobutyl ketone (MIBK) and 50% cyclohexanone. Toluene and xylene have also been added as co-solvents in smaller proportions (30%). However, the rain erosion data from lacquers containing 40:30:30 MIBK: toluene: xylene shows this system to be poorer than other solvent systems. In this case, the more volatile MIBK probably volatilized faster than the aromatic solvents. Since the polymer is less soluble in the aromatics, some polymer separated out of the still-fluid lacquer. The partial precipitation gave a non-homogeneous film which weakened erosion properties.

Further studies showed that the complete removal of ketones is very difficult because of the mutual attraction between the polar groups of the solvent and polymer. Films dried for 20 days still gave positive phenylhydrazine tests on ether extracts. Solvent retention results in an increase in compliance as shown by the creep diagram. (Fig.V) Another effect of solvent retention is the retardation of air cures by the association of solvent with the reactive groups of the curing agent.

The solubility of CMA polymers in ketones is enhanced by the addition of Tuads on the mill. Also, the milling itself is a factor which must be considered, since increased milling yields a more soluble, gel-free polymer. Moreover, the tensile strengths increase



with milling time without any appreciable change in elongation and set properties. However, excessive milling causes polymer degradation followed by inferior physical properties. However, even short milling with very tight rolls causes marked degradation. Hence, the milling variable is one of the hardest to control and is responsible for variations in lacquer and film properties of similar polymers. It is the purpose of the sulfur modifier to eliminate gel from the gum specimens and thus reduce the amount of milling required to obtain adequate solubility. In chloroprene methacrylamide polymers, the use of t-octyl and t-dodecyl mercaptan as modifiers gave desirable results. Sulfur was similarly effective for the CMA polymers.

2. The Stability of the Lacquers

When no curing agents are added, the solutions are stable for several months, and if thickening of the lacquer does occur, it can be remedied by adding more solvent. Apparently no loss in physical properties results from this procedure. However, if curing agents are added before storage, the period of stability is reduced and irreversible gel is noticed after a week. Additional ball-milling does not break up the grainy solution, so it is impossible to obtain a smooth, homogeneous coating. In order to achieve reasonable storage or shelf lives for the CMA lacquers, it is necessary to add the curing agent immediately prior to use.

III. SUMMARY

A study of chloroprene polymers has shown that it is difficult to correlate any physical property of a coating with its rain erosion resistance. The unfortunate lack of correlation stems from the fact that the physical tests are not related to two major factors affecting rain erosion protection; namely, smoothness of the coating and homogen-

city of the polymer. Experiments on uncoated aluminum indicate that the erosion rate increases exponentially with respect to roughness of the leading edge. For this reason, it is imperative that the application procedure leaves a smooth surface. Likewise, a heterogeneous surface will have spots of extreme weakness as well as areas of high strength. The weak spots cause early failure and lead to initiation of erosion which, once begun, appears to be autocatalytic. The CMA polymer tends to form bubbles when immersed in water. These bubbles result from flaws in the surface and the warped polymer flakes off before true erosion takes place. The successful commercial coatings show a gradual erosion which starts at the high speed end and works down to the low speed end; the suspected reason for this effect is the superior surface texture of the commercial coatings.

Despite the inferior surface characteristics of CMA, this polymer gives erosion times comparable to Goodyear's and Gate's coatings. The suspected reason for CMA's success is its excellent tensile strength and elastic behavior. As of yet, the bubble deficiency has not been corrected. In general, additives lowered the strength and elasticity of the polymer and as a result they are undesirable. The newly developed chloroprene-methacrylamide polymer has shown excellent results in rain erosion tests and surpass CMA coatings in some instances.

Table V

Cornell Series No. 9

Specimen No.	Polymer No.	Additives	Curing Agents	Curing Conditions	Primer	No. of Coats	Approx. Thickness in Mils
9A	A-37 ¹	2 pts Royal Spectra Carbon Black	5 pts ZnO	Room Temp.	Bostik	13	8.5
9B	AK-20 ²	None	10 pts Zimate ³ / 2 pts DADPM ⁴	1 hr. at 120°C	C-MA	14	8.0
9C	AK-20	2 pts Royal Spectra	2 mls. Accel 983-C ⁵ per 2 gms polymer	Room Temp.	C-MA	14	8.0
9D	AK-20	None	5 pts ZnO	Room Temp.	Bostik	14	8.5
9E	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	Room Temp.	Bostik	15	9.0
9F	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	Room Temp.	C-MA	12	7.5
9G	AK-20	5 pts Hydrophobic Silica	5 pts ZnO	Room Temp.	Bostik	12	7.5
9H	AK-20	None	1 pt MgO	Room Temp.	C-MA	13	8.0
9I	AK-20	None	2 mls 983-C/2gm Polymer / 4 pts DADPM	Room Temp.	Bostik	15	9.0
9J	AK-20	None	2 mls 983-C/2gm polymer / 4 pts DADPM / 2 pts ZnO	Room Temp.	Bostik	14	9.0

1. C-MA Copolymer with conversion of 55.0% and acid content of 12.7%.
2. C-MA Copolymer with conversion of 52.5% and acid content of 11.8%.
3. Zinc diethyl dithiocarbamate.
4. p-p'-Diaminodiphenylmethane
5. Goodyear Accelerator 983-C

Table VI

A.S.R.L. No.	Topcoat Composition	Curing Agents	Curing Conditions	Tensile Strength	Topcoat Thickness
10-A	Chloroprene-methacryl- amide copolymer	.9 ml 983-c/gm polymer	Room Temp.	3060	ca. 8
10-B	"	6 pts Et-Zimate plus	2 hrs @120°C	3520	ca. 8
10-C	"	2 pts MgO+2 pts Sulfur	2 hrs @120°C	4150	ca. 8
10-D	C-MA A-37 ²	6 pts p-phenylene diamine	Room Temp.	5780	ca. 8.5-9.0
10-E	"	6 pts DPG	"	4400	ca. 8
10-F	"	6 pts DPG plus 0.5pt paraffin	"	ca. 3600	ca. 8
10-G	"	3 pts DPG plus 3 pts Benzidine	"	4500	ca. 8
10-H	"	6 pts DADPM	"	3230	ca. 3
10-I	Gates ³	6 pts o-phenylene diamine	"	3030	ca. 8
10-J	Hypalon S-2 ⁴	3 pts DPG+3 pts DADPM + 3 pts MBT	"	2810	ca. 10
10-K	Gates	6 pts p-phenylene diamine	"	3200	ca. 9.0-9.5
10-L	CMA A-37	6 pts Benzidine	"	4370	ca. 7.5
10-M	"	10 pts Benzidine	"	4640	ca. 8
10-N	"	6 pts o-phenylene diamine	"	2900	ca. 8

Notes

1. 10% methacrylamide at 62% conversion
2. Chloroprene-methacrylic acid copolymer of 55.04% conversion and an acid content of 12.7%
3. Gates Engineering Company's commercial polymer lacquer N-79
4. Dupont's chlorosulfonated polythene polymer dissolved in methylethyl ketone and toluene.

Table VII

Creep Behavior of the C-MA Copolymers

Run No.	Specimen	Curing System ¹	Cure	Aging Days	Load Kg/cm ²	1 min. Comp.	10 min. Comp.
2	Gates		R.T.	7	3.38	1.15	1.3
3	C-MA-T	10-Zimate, 2-DADPM	1 hr. at 120°C	7	9.18	8.5	12.9
7	C-MA-T	10-Zimate, 2-DADPM	"	64	9.85	6.4	8.6
6	Goodyear		R.T.	6	33.1	0.15	0.22
8	AK-20	10-Zimate, 2-DADPM 10-Hydrophobic Silica	1 hr. at 120°C	60	6.20	3.2	4.5
9	AK-20	10-Zimate, 2-DADPM 20-Hydrophobic Silica	"	60	7.44	0.8	1.75
10	9E		R.T.	18	8.81	10.5	18.7
11	9A		R.T.	18	8.12	3.6	4.7
12	9F		R.T.	20	8.32	~ 16	~ 30
13	9J		R.T.	19	9.45	7.4	10.3
14	9D		R.T.	14	7.63	3.5	5.3
15	9C		R.T.	23	5.63	~ 18.5	~ 36
16	9B		R.T.	20	5.89	7.2	9.9

1. Curing systems for the 9th Rain Erosion test series indicated in Table V

Table VIII

Cornell Series No. 9

Specimen No.	Polymer No.	Additives	Curing Agents	Primer	Time to erode through coating of test	Total Time of test
9A	A-37 ¹	2 pts Royal Spectra Carbon Black	5 pts ZnO	Bostik	20 min.	50 min.
9B	AK-20 ²	None	10 pts Zimate ³ + 2 pts DADPM ⁴	C-MA	30 min.	50 min.
9C	AK-20	2 pts Royal Spectra	2 mls. Accel 983-C ⁵ per 2 gms polymer	C-MA	10 min.	50 min.
9D	AK-20	None	5 pts ZnO	Bostik	Film began to peel off in layers after 10 min.	50 min.
9E	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	Bostik	30 min.	50 min.
9F	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	C-MA	40 min.	70 min.
9G	AK-20	5 pts Hydrophobic Silica	5 pts ZnO	Bostik	20 min.	50 min.
9H	AK-20	None	1 pt MgO	C-MA	20 min.	60 min.
9I	AK-20	None	2 mls 983-C/2 gm Polymer + 4 pts DADPM	Bostik	60 min.	80 min.
9J	AK-20	None	2 mls 983-C/2gm poly-mer + 4 pts DADPM + 2 pts ZnO	Bostik	20 min.	50 min.

For footnotes see next page

Table VIII-(Continued)

1. C-MA Copolymer with conversion of 55.0% and acid content of 12.7%.
2. C-MA Copolymer with conversion of 52.5% and acid content of 11.8%.
3. Zinc diethyl dithiocarbamate.
4. p-p'-Diaminodiphenylmethane.
5. Goodyear Accelerator 983-C.
6. 9B cured at 120° C. for 1 hour, All others room temperature cures.

TABLE IX

RESULTS OF 10th SERIES OF RAIN-EROSION TESTS

SPECIMEN NO.	COPOLYMER	ACCELERATOR	APPROXIMATE THICKNESS OF FILM (MILS)	TIME TO ERODE THRU COATING (MINUTES)	TOTAL TIME OF TEST (MINUTES)	TENSILE STRENGTH (PSI)
10 A	Chloroprene Methacrylamide	✓ .9 ml of Goodyear 983-C/gm of Polymer R. Temp.	8	60	140	3080
10 B	Chloroprene Methacrylamide	✓ .9 ml of Goodyear 983-C/gm of Polymer	10	80	235	3520
10 C	Chloroprene Methacrylamide	✓ 6 pts Et Zimate 2 pts MgO 2 pts 3	9	40	100	4180
10 D	A-37	✓ 6 pts p-Phenylene diamine	9	10	15	5780
10 E	A-37	✓ 6 pts DPG	8	10	15	4400
10 F	A-37	✓ 6 pts DADPM / 0.5 pt Paraffin	8	3	10	3600
10 G	A-37	✓ 3 pts DPG / 3 pts Benzidine	8	15	25	4800
10 H	A-37	✓ 6 pts DADPM	8	7	10	3230
10 I	Gates	✓ 6 pts O-Phenylene diamine	8	36	45	3030
10 J	Hypalon	✓ 3 pts DPG; / 3 pts MBT; ✓ 3 pts DADPM	10	15	20	2810
10 K	Gates	✓ 6 pts p-Phenylene diamine	10	76	96	3200
10 L	A-37	✓ 6 pts Benzidine	8	7	11	4370
10 M	A-37	✓ 10 pts Benzidine	8	7	10	4640
10 N	A-37	✓ 6 pts O-Phenylene diamine	8	7	10	2900
B & C were cured for two hours at 120° C. All other cures were at room temperature. Bostick primer was used on Specimens A, B, C, I, J, and K. Standard CMA primer was used on all other specimens.						

Figure VI

The Creep Apparatus.

